

CATALYTIC SYSTEM AND METHOD FOR REDUCING PERCHLORATE ION

BACKGROUND OF THE INVENTION

5 1. Field of the Invention

The present invention relates to catalytic systems for enhancing the reduction of the perchlorate ion and methods of reducing the perchlorate ion. The invention is particularly useful in the areas of perchlorate transformation and removal from the environment.

10 2. Description of the Related Art

Perchlorate (ClO_4^-) originates as a contaminant in the environment from the solid salts of ammonium or sodium perchlorate. Most perchlorate salts are quite soluble in water. The resultant anion (ClO_4^-) is exceedingly mobile in aqueous systems. Because of its resistance to reaction with other available constituents,
15 perchlorate can persist for many decades under typical groundwater and surface water conditions. Perchlorate salts are manufactured for use as an oxygen-adding component in solid propellant for rockets, missiles, fireworks and certain munitions. Since it has a limited shelf life, inventories of ammonium perchlorate must be periodically replaced with a fresh supply. Thus, large volumes of the compound have
20 been disposed of since the 1950's in Nevada, California, Utah, and probably other states. As a consequence, contamination of the water supply by perchlorate is becoming a serious human health concern.

The danger to health presented by perchlorate relates to its effect on the thyroid gland. The perchlorate ion acts as a competitive inhibitor of iodide anion
25 uptake by the thyroid gland, which results in reduced thyroid hormone production. Thyroid hormone deficiencies can cause abnormal metabolism, growth and development.

Although thermodynamically a powerful oxidant, perchlorate ion is unreactive to most reducing agents when in dilute aqueous solution, because perchlorate redox reactions are exceedingly slow. These properties make developing treatment technologies difficult, especially at low concentration levels.

5 Such normally active reductants as chromous ion, stannous ion and uranous ion are inert towards perchlorate ion in aqueous media. A few simple inorganic species do reduce perchlorate ion in aqueous media, more or less sluggishly. Among these are titanous ion (Ti^{3+}), Mo^{III} and Ru^{2+} . Jeske et al, *Inorg. Chem.*, 33:47, 1994. Also, V^{2+} and V^{3+} react with perchlorate ion in aqueous media, but only at high
10 temperatures and at low rates. King et al, *J. Phys. Chem.*, 58:29, 1954. It has been reported that oxyanions including molybdate, tungstate, and niobate, are capable of catalyzing the reduction of perchlorate ion by stannous ion under some conditions. Haight, Jr. et al, *J. Am. Chem. Soc.*, 74:6056-6059, 1952; Haight, Jr. et al, *J. Am. Chem. Soc.*, 76:4718-4721, 1954. More recently, the powerful oxygen-transfer agent
15 $(\text{CH}_3)_2\text{ReO}_2$ has been shown to react with perchlorate ion rather rapidly. Abu-Omar et al, *Inorg. Chem.*, 34:6239-6240, 1995. The reaction of Ru^{2+} with perchlorate is fairly slow, but the rate-limiting step is replacement of coordinated water by the anion, with all subsequent steps leading to production of chlorate ion being quite rapid. Kallen and Early, *Inorg. Chem.*, 10:1152, 1971; 98:151, 1982.

20 Other methods attempted for the removal of perchlorate from water supplies include the use of perchlorate destroying bacteria, reverse osmosis and ion-exchange processes. These methods, however, have had limited effectiveness and/or are excessively expensive to implement at the industrial level. As well, most of the present techniques employed in perchlorate environmental management are based on
25 the removal of perchlorate ions from area where they may pass through to the open environment and confining those ions in more secluded and controlled storage facilities. However, separating perchlorate ions from the open environment for more controlled storage is of limited benefit due to the added cost of storing the perchlorate ions and preventing their passing into the open environment. A much
30 more desirable approach is to transform the potentially harmful perchlorate ions into less harmful or safer chemical species. It is further desirable to develop techniques

that are based on transforming the perchlorate ions into less harmful species and that can be easily implemented at the industrial level in a cost effective manner.

SUMMARY OF THE INVENTION

The present invention relates to a catalytic system and methods and processes based thereon for the effective transformation, and optionally, the removal of perchlorate ions that may be present in the open environment or in facilities for the storage of perchlorate-containing waste. The catalytic system of the invention allows the implementation of perchlorate transformation processes at the industrial level in a cost effective manner.

One aspect of the present invention provides a catalytic system for enhancing perchlorate ion reduction. The catalytic system comprises one or more titanium assemblies, each titanium assembly comprising two or more titanium cations, wherein the cations in the assembly are capable of transferring electrical charge to the perchlorate ion, thereby reducing the oxidation state of the chlorine center of the perchlorate ion, and wherein the titanium cations and perchlorate ion are in a moderately polar or partially structured solvent environment. Preferably, the titanium assembly is a dimer of titanium cations and the moderately polar environment has a polarity that is approximately equivalent to that of ethyl alcohol.

In one embodiment, the invention provides a catalytic system wherein the moderately polar environment comprises a non liquid phase comprising a core and a surface, wherein the surface comprises a functional group having a polarity equivalent to the polarity of ethyl alcohol. Preferably, the core is hydrophobic, for example a core comprising polyvinyl chains. Other cores that can be used in conjunction with the present invention silica gel and zeolitic material or any other support capable of supporting a functional group at the surface of the support, wherein the functional group is capable of promoting the interaction between the perchlorate ions and the titanium assembly. Preferably, the functional group on the surface of the core comprises a hydroxyl group.

In another embodiment, the present invention provides a catalytic system further comprising a ligand in interaction with the titanium assembly.

One aspect of the invention provides the ligand 11, 23-dihydroxycarbonyl-25, 26-dihydroxy-3, 7, 15, 19-tetraazatricyclo[19. 3. 1. 19. 13]hexacosa-1(25), 9(26), 10, 12, 21, 23-hexaene, hereafter TADP3-(COOH)₂, which is a ligand that was designed in conjunction with the catalytic system of the subject invention.

5 In addition to novel ligand TADP3-(COOH)₂, the present invention can be practiced with any conventional ligand capable of enhancing the formation of multinuclear reduced titanium species. Exemplary ligands include TADP3; 6-amino-6-(4-aminobenzyl)-1,4,8,11 tetraazacyclotetradecane; 1,4,7-triazacyclononane-N,N',N''-triacetic acid; N,N',N'-tris(2-pyridylmethyl)-cic,cis-1,3,5-
10 triaminocyclohexane; α -cyclodextrin; saphyrins and porpherin analogues thereof; HEDTA; DADP3; and CYCAPAB. The chemical structures of these ligands provided in Figure 4.

Another aspect of the present invention provides a method of reducing perchlorate ions in dilute aqueous solutions. The method comprises contacting the
15 perchlorate ions with a catalytic system comprising one or more titanium assemblies, each titanium assembly comprising two or more titanium cations, wherein the cations in the assembly are capable of transferring electrical charge to the perchlorate ion, thereby the oxidation state of the chlorine center of the perchlorate ion, and wherein said titanium cations and perchlorate ions are in a moderately polar environment,
20 which is particularly effective in promoting the interaction between the titanium assembly and the perchlorate ion.

Another aspect of the invention provides a process of removing perchlorate ions from water, wherein the process comprises reducing perchlorate ions by contacting the perchlorate ions with a catalytic system comprising one or more
25 titanium assemblies, each titanium assembly comprising two or more titanium cations, wherein the cations in the assembly are capable of transferring electrical charge to the perchlorate ion, thereby reducing the oxidation state of the chlorine center of the perchlorate ion, and wherein the titanium cations and perchlorate ion are in a moderately polar environment.

30 Yet another aspect of the invention provides a process of removing perchlorate ions from rocket fuel waste, wherein the process comprises reducing perchlorate ions

by contacting the perchlorate ion with a catalytic system comprising one or more titanium assemblies, each titanium assembly comprising two or more titanium cations, wherein the cations in the assembly are capable of transferring electrical charge to the perchlorate ion thereby reducing the oxidation state of the chlorine center of the perchlorate ion, and wherein the titanium cations and perchlorate ion are in a moderately polar environment.

The catalytic system of the invention can be regenerated by restoring the electrical charge on the titanium assembly. Restoring the electrical charge on the titanium assembly can be achieved by any means known in the art. Preferred means for restoring the electrical charge on the titanium assembly to regenerate the catalytic system of the invention include electrical charge transfer to the titanium assembly through an electrochemical reaction, photochemical reaction or by electrical current.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates the structure of $\text{Ti}(\text{HEDTA})(\text{H}_2\text{O})$.

Figure 2 illustrates the structure of $\text{Ti}(\text{HEDTA})(\text{H}_2\text{O})$.

Figure 3 illustrates the structure of the complex $[\text{Cu}(\text{DMAEP})\text{OH}]_2(\text{ClO}_4)_2$.

Figure 4 are structural representations of ligands.

Figure 5 shows absorption spectra of Ti^{III} and Ti^{III} complexes. $\mu=3.6 \text{ M}$ (LiCl); $T=25^\circ\text{C}$ $[\text{H}^+]=68 \text{ mM}$.

Figure 6 shows the dependence of pseudo-first order rate constant on $[\text{ClO}_4^-]$. $\text{L}=\text{HEDTA}$. $[\text{L}]=6.2 \text{ mM}$; $[\text{Ti}^{\text{III}}]=8.8 \text{ mM}$; $[\text{H}^+]=105 \text{ mM}$. $m=4.5 \text{ M}$, $T=24.8^\circ\text{C}$.

Figure 7 shows the dependence of observed rate constants for the reduction of perchlorate ions by titanous complexes on acidity. $T=24.8^\circ\text{C}$, $\mu=4.40 \text{ M}$, $[\text{ClO}_4^-]=0.50 \text{ M}$, $[\text{Ti}^{\text{III}}]=8.2 \text{ mM}$. ● Ti^{III} complex of ligand TADP3; ▲ Ti^{III} complex of ligand CYCAPAB; ★ Ti^{III} complex of ligand DADP3; ◆ Ti^{III} complex of ligand HEDTA; ▲ Uncomplexed Ti^{III} (right scale). Dotted lines correspond to $k = k_0 + k'[\text{H}^+]^2$ where: ● $k_0 = 330 \text{ (s}^{-1}\text{)}$, $k' = 2.6 \times 10^{-3} \text{ (s}^{-1} \text{ mM}^{-2}\text{)}$; ▲ $k_0 = 172 \text{ (s}^{-1}\text{)}$, $k' = 1.4 \times 10^{-3} \text{ (s}^{-1} \text{ mM}^{-2}\text{)}$; ★ $k_0 = 105 \text{ (s}^{-1}\text{)}$, $k' = 8.6 \times 10^{-4} \text{ (s}^{-1} \text{ mM}^{-2}\text{)}$; ◆ $k_0 = 40 \text{ (s}^{-1}\text{)}$, $k' = 1.1 \times 10^{-3} \text{ (s}^{-1} \text{ mM}^{-2}\text{)}$; ▲ $k_0 = 1.3 \text{ (s}^{-1}\text{)}$, $k' = 2.3 \times 10^{-5} \text{ (s}^{-1} \text{ mM}^{-2}\text{)}$

Figure 8 shows the dependence of pseudo-first order rate constant on $[\text{Ti}^{\text{III}}]_{\text{TOT}}$. $\text{L}=\text{HEDTA}$. $[\text{L}]=6.2 \text{ mM}$; $[\text{ClO}_4^-]=0.50 \text{ M}$; $[\text{H}^+]=0.19 \text{ M}$; $\mu=4.5 \text{ M}$; $T=24.7^\circ\text{C}$. Red circles, simulation using IBM-Almaden Chemical Kinetics Simulation Program with $k_{1f}=1000 \text{ M}^{-1} \text{ sec}^{-1}$, $k_{1r}=2000 \text{ sec}^{-1}$, $k_{2f}=1000 \text{ M}^{-1} \text{ sec}^{-1}$, $k_{2r}=0.1 \text{ sec}^{-1}$ and $k_3[\text{ClO}_4^-]=0.1 \text{ sec}^{-1}$.

Figure 9 shows the synthetic scheme for the immobilization of $\text{TADP3}(\text{COOH})_2$ on Polyvinyl.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

“Titanium assembly” is used herein to refer to any multi-nucleus titanium species capable of donating electrons to the perchlorate ion. In this regard, any titanium species having an oxidation state lower than +IV is suitable for use in conjunction with the subject invention. In particular, assemblies of two or more $\text{Ti}(\text{III})$ are highly suitable for use in conjunction with the subject invention.

The reaction of Ti^{3+} with perchlorate is of considerable interest since this reaction is faster than that of other first-row reductants but much slower than replacement of water coordinated to the cation, so that the rate limiting step must involve the redox change. Since titanium compounds are readily available and cheap, identifying effective catalysts based on the Ti^{III} -perchlorate ion reaction is of considerable practical value.

The focus of the subject application is a catalytic system based on the titanium-perchlorate ion reaction. Specifically, it has been discovered that providing titanium ions in the form of an assembly containing two or more titanium cations is very effective in transferring electrical charge from the titanium assembly to the chlorine center in the perchlorate ion.

The transfer of the charge from the titanium assembly to the perchlorate ion is dramatically enhanced when the titanium assembly and the perchlorate ion are disposed in an environment which does not form an organized structure. That is, in a polar environment, for example in water, the solubility of perchlorate ion is fostered by its ability to disrupt the structure of water. This disruption is believed to be

associated with a favorable entropic effect which enhances the solvability of the perchlorate ion in water. The enhanced solvability of the perchlorate ion in water makes it difficult to "extract" the perchlorate ion from its water environment thereby making it difficult for the titanium cations to interact with the perchlorate ion, which
5 may explain the very slow electron transfer from titanium cations to the perchlorate ion in water.

By the present invention, it has been determined that a polymeric form of Ti^{III} binds perchlorate ion in such a way as to distort the perchlorate ion away from tetrahedral symmetry. This polymeric form of Ti^{III} is preferably a dinuclear Ti^{III}
10 species. It is believed that this distortion of perchlorate then allows for its conversion to chlorate, and subsequent degradation to chloride.

Thus, in one embodiment the present invention provides a new catalytic system for reducing perchlorate ions and thereby limiting their harmful effects on the environment and facilitating their removal therefrom. The catalytic system is based
15 on a titanium assembly of two or more titanium cations in an appropriate medium. The titanium assembly is associated with the perchlorate ion to favor the transfer of electronic charge from the titanium assembly to the perchlorate ion, thereby reducing the perchlorate ion to a species having a chlorine center of an oxidation state that is lower than the oxidation state of the chlorine center in the perchlorate ion. Preferably,
20 the titanium assembly is a dimer of titanium cations and the moderately polar environment comprises ethyl alcohol or another material with similar properties to those of ethyl alcohol with respect to the interaction between the titanium assembly and the perchlorate ion.

In the catalytic system of the invention, the titanium cations are in a
25 moderately polar environment. In a preferred catalytic system according to the invention, the moderately polar environment comprises a non liquid phase comprising a core and a surface, wherein the surface comprises a functional group having a polarity equivalent to the polarity of ethyl alcohol. Preferably, the core is hydrophobic, for example, the core may comprise polyvinyl chains. Preferred non-
30 hydrophobic cores that can be used in conjunction with the present invention include silica gel, zeolitic materials and other supports that may have a functional group

which can mimic the effect of the presence of ethyl alcohol on the interaction between the titanium assembly and the perchlorate ion. Such functional groups include the hydroxyl group and other groups having similar polarity properties.

More preferably, a catalytic system according to the invention further
 5 comprises a ligand in interaction with the titanium assembly. The presence of a ligand in the catalytic system according to the invention provides numerous advantages. One advantage relates to the role played by the ligand in the formation of the assembly of titanium cations, thereby enhancing the possibility of electron transfer between the titanium assembly and the perchlorate ion. Another advantage relates to
 10 the stabilization of the (reduced) oxidation state of the titanium cations in the assembly in the presence of oxygen or other strong oxidant agents. While the catalytic systems of the invention provide titanium assemblies containing titanium species in a reduced state which are less prone to oxidation by oxidizing agents, the presence of the ligand further stabilizes the titanium in the assembly in a reduced
 15 state, which in turn allows the use of the catalytic system of the invention in conditions that may include oxygen or other oxidizing agent. This greatly simplifies the systems required for using the catalytic system of the invention in an industrial environment.

As discussed in detail below, a ligand has been developed based on the broad
 20 concept of the subject invention. In investigating the effect of various ligands on the effectiveness of the catalytic system of the invention a new ligand that fosters the formation of the titanium assemblies of the invention and stabilizes those assemblies against oxidizing agents has been designed. The new ligand is 11, 23-dihydroxycarbonyl-25, 26-dihydroxy-3, 7, 15, 19-tetraazatricyclo[19. 3. 1. 19.
 25 13]hexacos-1(25), 9(26), 10, 12, 21, 23-hexaene.

In addition to novel ligand TADP3-(COOH)₂, the present invention can be practiced with any conventional ligand capable of enhancing the formation of multinuclear reduced titanium species. Exemplary ligands include TADP3; 6-amino-6-(4-aminobenzyl)-1,4,8,11 tetraazacyclotetradecane; 1,4,7-triazacyclononane-
 30 N,N',N''-triacetic acid; N,N',N'-tris(2-pyridylmethyl)-cis,cis-1,3,5-

triaminocyclohexane; α -cyclodextrin; saphyrins and porpherin analogues thereof; HEDTA; DADP3; and CYCAPAB.

Another aspect of the present invention provides a method of reducing perchlorate ions in dilute aqueous solutions. The method comprises contacting the perchlorate ions with a catalytic system comprising one or more titanium assemblies, each titanium assembly comprising two or more titanium cations, wherein the cations in the assembly are capable of transferring electrical charge to the perchlorate ion, thereby the oxidation state of the chlorine center of the perchlorate ion, and wherein said titanium cations and perchlorate ions are in a moderately polar environment, which is particularly effective in promoting the interaction between the titanium assembly and the perchlorate ion.

Based on the new catalytic system of the invention, a particularly efficient method of reducing perchlorate ions, particularly in a dilute state is provided. The method comprises contacting the perchlorate ions with the catalytic system of the invention.

The catalytic system of the invention and the method of reducing perchlorate ion based thereon are advantageously implemented in industrial processes for the transformation and/or removal of perchlorate ions from industrial effluents and facilities wherein perchlorate-containing industrial waste is stored. These processes are based on reducing perchlorate ions by contacting the perchlorate ions with a catalytic system according to the invention.

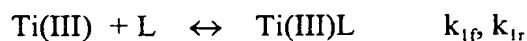
As discussed above, in conjunction with the subject invention, several new ligands were prepared, TADP3 (25, 26-dihydroxy-3, 7, 15, 19-tetraazatriciclo[19. 3. 1. 19. 13] hexacosa-1 (25), 9 (26), 10, 12, 21, 23 hexaene); CYCAPAB (6-amino-6-(4-aminobenzyl)-1, 4, 8, 11-tetraazacyclotetradecane); TADP3(COOH)₂ DADP3 (N,N'-propylene-bis-(2 hydroxybenzylamine)). Ti(III) complexes of these ligands (and of HEDTA, hydroxyethylethylenediaminetetraacetic acid) were examined.

In the presence of any these ligands the UV-visible spectrum of Ti(III) (in dilute, aqueous acid at 25C in the absence of dioxygen) is shifted and made more intense, and a peak at 738 nm becomes more prominent (Figure 5). In dilute acid in the absence of dioxygen, these spectra fade more or less rapidly on addition of

perchlorate ion. In all cases studied, the peak absorbance showed an exponential time-decay, yielding a pseudo-first order rate constant, k . The initial chlorine-containing product of the reaction between Ti(III) and perchlorate ion was found to be chlorate ion. When Ti(III) is in excess, the eventual product was found to be chloride ion.

At constant acid and Ti(III) concentrations, all reaction rates were proportional to perchlorate concentration (**Figure 6**). Pseudo-first order rate constants increased as $[H^+]$ increased (**Figure 7**). Curvature in the rate *versus* acid concentration plots indicates some contribution from a rate-law term second order in $[H^+]$. At $[H^+] = 432$ mM, $Ti(III) = 8.2$ mM and perchlorate = 0.50 M, at ionic strength 4.8 M and 25C, relative rate constants (sec^{-1}) were found to be: TADP3 (158) > CYCAPAB (86) > DADP3 (48) \geq HEDTA (44) > no ligand (1). This order is also the order of intensity of absorbance at 778 nm. Since the 778 peak has previously been identifiedⁱ as being characteristic of dinuclear species, this result suggests that a complex containing one perchlorate, two titanium(III) ions, and two protons is involved in or prior to the rate determining step of Ti(III)—perchlorate reaction. Complexes of copper (II) that have closely related structures have been isolated from ethanolic solutions.

For all ligands studied, pseudo-first order rate constants of the Ti(III)-perchlorate reaction depend linearly on the concentration of Ti(III). This unusual behavior can be modeled (**Figure 8**) (using the IBM-Almaden Chemical Kinetics Simulation program) by a mechanism involving a dinuclear intermediate.



The success of this modeling tends to substantiate the conclusion that was based on the relationship between rate of reaction and absorbance at 778 nm — that a dinuclear intermediate or transition state is implicated in the reaction mechanism. On this basis, the reason that some ligands are more effective catalysts than others is that the more-effective ligands favor formation of the dinuclear species to a greater degree than do the less-effective ligands. It is believed that the Ti^{III} -perchlorate reaction is more rapid in methanol or media that mimic the properties associated with the effect of the presence of ethanol on the interaction between the titanium assembly of the

invention and the perchlorate ion due to the enhancing effect of such media on the association of the perchlorate ion and the titanium assembly of the invention.

We prepared another novel ligand TADP3-(COOH)₂ (11, 23-dihydroxycarbonyl-25, 26-dihydroxy-3, 7, 15, 19-tetraazatricyclo[19. 3. 1. 19. 13]hexacosa-1(25), 9(26), 10, 12, 21, 23-hexaene). This ligand is similar to TADP3 (the most active catalyst among the ligands we studied) but also carries two axial carboxyl groups to facilitate linking that ligand to a semi-solid support by the standard method shown in **Figure 9**.

Polyvinyl alcohol (50 < MW < 85 kDal, 97% hydrolyzed) was used as a semi-solid support to demonstrate the claims of the preliminary application. De-oxygenated mixtures that were 60 mM in Ti(III), 0.17 M in HCl, 2.3 M in LiCl and contained 0.25 g of polyvinyl alcohol per ml of mixture, retained the purple color of Ti(III), unchanged in intensity, for periods of at least two weeks at 25C. This indicates that oxidation of Ti(III) either did not occur or occurred very slowly. De-oxygenated mixtures that were 60 mM in Ti(III), 0.17 M in HCl, 2.8 M in LiClO₄ and contained 0.25 g of polyvinyl alcohol per ml of mixture faded completely in 45 +/- 10 minutes at 25C. Substitution of perchlorate for chloride brings about rather rapid decolorization of Ti(III). The rate of the corresponding reaction in the absence of PVA can be calculated from the observed linear dependence of rate on perchlorate concentration (**Figure 6**). This calculation, combined with the experimental results, shows that the rate of the Ti(III)-perchlorate reaction in the presence of polyvinyl alcohol is approximately forty times faster than the rate of the corresponding reaction, under the same conditions, in the absence of polyvinyl alcohol.

We attached TADP3-(COOH)₂ to polyvinyl alcohol using the method shown in **Figure 9**. Spectrophotometric analysis showed that a significant amount of the PVA molecules carried a TADP3-(COOH)₂ addend molecule. In the presence of polyvinyl alcohol that has been modified by attachment of TADP3-(COOH)₂ (in amount equivalent to ~4 mM), 60 mM Ti(III) is decolorized within 45 +/- 10 minutes at 25C by 0.028 M lithium perchlorate (in 0.17 M HCl at 25C). These results demonstrate that a substantially more rapid redox reaction occurs between Ti(III) and perchlorate when a ligand that fosters formation of dinuclear Ti(III) species is

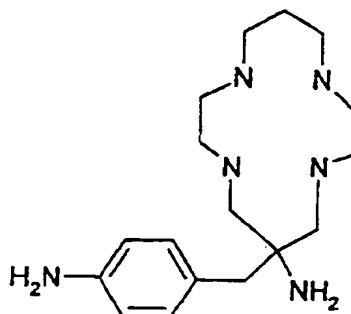
attached to the polyvinyl alcohol than when unmodified polyvinyl alcohol is present (other conditions being the same). As mentioned above, and shown in **Figure 6**, Ti(III)-perchlorate reactions have rates that are linearly dependent on perchlorate concentration. The perchlorate concentration that would cause complete reaction
5 between Ti(III) and perchlorate in 45 +/- 10 minutes at 25C is about forty-eight times larger in the case of the unmodified polyvinyl alcohol than in the case of the ligand-modified polyvinyl alcohol. This demonstrates that the rate of reaction involving the ligand-modified polyvinyl alcohol is approximately fifty times faster than that involving unmodified polyvinyl alcohol.

10 In accordance with the present invention, the reduction of perchlorate ion by titanous ions is catalyzed by semi-solid media that provide a local reaction environment of moderate polarity, similar to that of ethanol. (Polyvinyl alcohol is used as example in this application.) As further claimed, suitable ligands (those that favor dinuclear complexes, as does TADP3) when bound to such a semi-solid medium,
15 further enhance the rate of the Ti(III)-perchlorate reaction. The overall rate enhancement, in the sample case, is a factor of approximately two thousand. Of this, a factor of forty comes from the effect of semi-solid support itself, and an additional factor of fifty from the ligand-modification of that support.

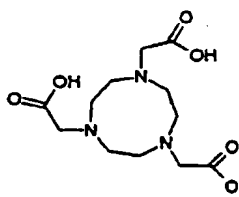
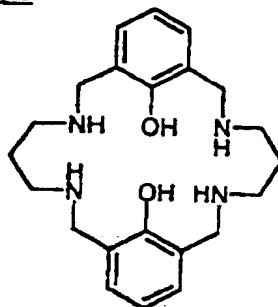
The scope of the subject invention, which is only limited by the appended
20 claims encompasses further modifications of the semi-solid support, the attached ligand, or the combination of support and ligand. It is expected that improvements in these three aspects of the invention will improve the catalysis by a factor of ten or more, we anticipate that other similar supports and related ligands would yield rates several orders of magnitude faster than the sample system we have investigated.
25 Methods and devices based on the new chemical principles described in this application can be used as the basis of expeditious and cost-effective methods (either batch or flow) to destroy surplus perchlorates.

Ligands which bind and stabilize chemical species that contain more than one titanium (III) center include the following:

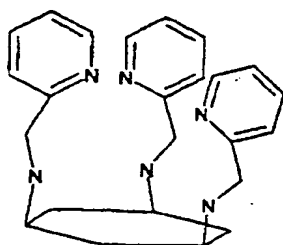
6-amino-6-(4-aminobenzyl)-1,4,8,11-tetraazacyclotetradecane



TADP3



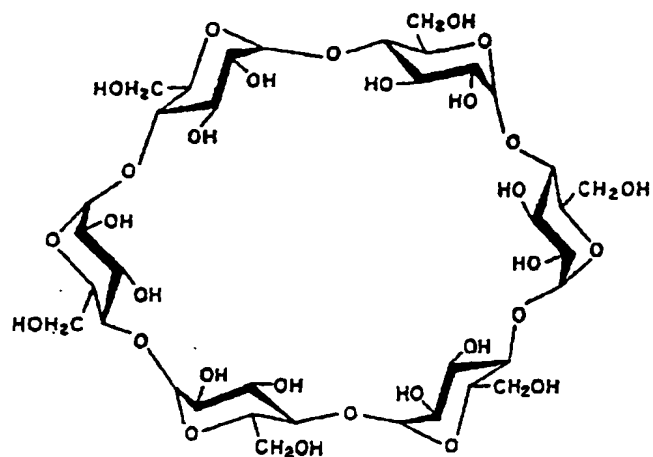
1,4,7-triazacyclononane-N,N',N''-triacetic acid
("tacnta")



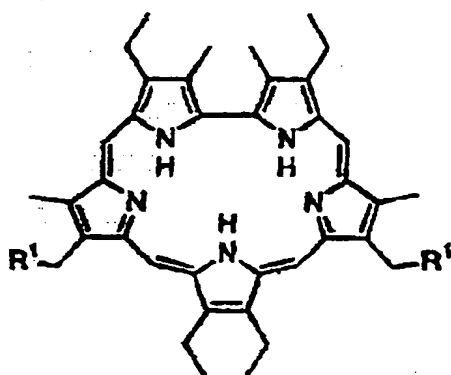
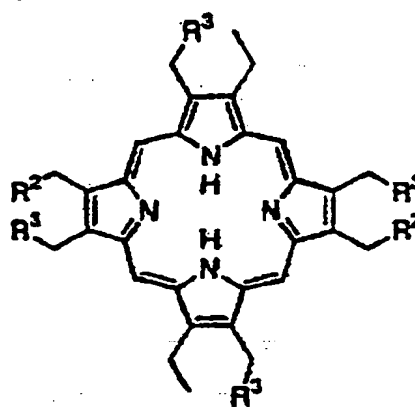
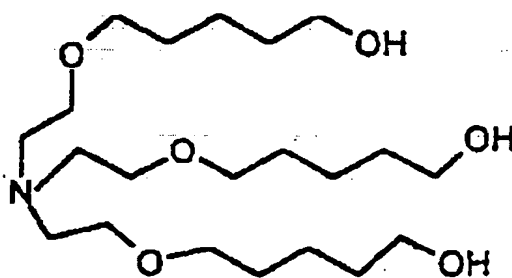
N,N',N''-tris(2-pyridylmethyl)-cis,cis-1,3,5-triaminocyclohexane

("tachpyr")

14

 α -cyclodextrin

Sapphyrins bearing different substituents (left) and their porphyrin analogues (right)

1 $R^1 = \text{CH}_2\text{CON}(\text{CH}_2\text{CH}_2\text{OH})_2$ 2 $R^1 = \text{CH}_2\text{CH}_2\text{OH}$ 3 $R^1 = \text{CH}_3$ 4 $R^2 = \text{CON}(\text{CH}_2\text{CH}_2\text{OH})_2, R^3 = \text{H}$ 5 $R^2 = R^3 = \text{CH}_3$ THE

The most preferable ligands are 6-amino-6-(4-aminobenzyl)-1,4,8,11-tetraazacyclotetradecane) and TADP3.

Preferably, the ligand-stabilized species of Ti^{III} are attached to a solid or semisolid support, the ligand being attached to the solid or semisolid support by chemical or physical means. The surface environment of the solid or semisolid support provides a mildly polar environment, comparable to the environment of aqueous ethanolic solutions. Preferably, the mildly polar environment provided is comparable to that provided by approximately 92% by volume of ethanol and approximately 8% by volume of water. The solid or semisolid support is any polymeric material suitable for water treatment which provides a mildly polar environment on its surface. Preferably, the solid or semisolid support is polyvinyl alcohol. The mildly polar environment provided by the solid or semisolid support facilitates association of perchlorate ions with two or more titanous ions, thereby accelerating the rate at which perchlorate ions are reduced and removed from aqueous solution.

The water supply is contacted with the ligand- Ti^{III} complex-solid/semisolid support at a rate such that perchlorate is degraded to an acceptably low level. The method can be performed, for example, via continuous flow, or by a batch-type exposure. If necessary, non-aqueous media can be added to facilitate the reaction. Such non-aqueous media include, for example, alcohols such as ethanol.

The ligand-stabilized species of Ti^{III} can be used to degrade perchlorate in water supplies, i.e., groundwater or water from other sources for drinking, agricultural or other purposes.

Example 1

Experimental

The structure of crystals containing the Ti^{III} and Ti^{IV} complexes of HEDTA have been determined. Both these complexes (Figure 1, Figure 2) contain seven-coordinated titanium, with the ligand alcohol group fully ligated in both cases.

Discussion of the visible spectrum of purple $Ti(aq)^{3+}$ (a d^1 ion) is one of the classic stories of inorganic chemistry. The long-wavelength shoulder on the main peak is traditionally assigned to Jahn-Teller distortion of the cation. We have found that, when aqueous $TiCl_3$ solutions are diluted with ethanol, the peak usually assigned

to d-d transitions of Ti^{3+} and its long wavelength shoulder persist, but an additional peak at 400 nm develops. When such solutions are treated with molecular sieves to remove water, the original peaks are much reduced or eliminated, and the 400 nm peak is greatly enhanced. In such dry solutions, the dependence of the intensity of the 400 nm peak on $[Ti^{III}]_{tot}$ does not follow Beer's Law: a dependence on a higher power of $[Ti^{III}]_{tot}$ is indicated. Increase of acid concentration, or addition of water, reduces the absorbance at 400nm and restores the original peaks.

When solutions containing perchlorate ion and small concentrations of water are reacted with solutions of $TiCl_3$ in dry ethanol, either in the presence of excess chloride ion, or of excess tosylate ion, the peak at 400 nm is rapidly bleached in a biphasic reaction. The more rapid phase encompasses >85% of the total absorbance change. Spectrophotometric titration after long reaction time shows that 0.15 ± 0.3 moles of perchlorate ion are reduced for each mole of Ti^{III} consumed. After linear correction for the slow second phase, the absorbance change that occurs during the rapid phase of the reduction is adequately fitted by a single exponential. In contrast to the acid-catalyzed behavior observed for the corresponding reaction in aqueous solution, the reaction between Ti^{III} and perchlorate in mainly ethanolic solution is base-catalyzed.

Results and Discussion

The structures (including bond lengths) of the red-purple $(Ti(HEDTA)(H_2O))$ complex and of its colorless deprotonated oxidation product are remarkably similar to each other. This indicates that, in this ligand environment at least, the activation barrier to redox reaction due to inner-sphere reorganization at the Ti center should be small. The barrier to the reduction of perchlorate ion must lie elsewhere.

The rate constant for the reduction of perchlorate ion in ethanol at 0.02M acid is much larger than the rate constant to be expected for the same acidity in the (acid catalyzed) reduction of perchlorate by $Ti(HEDTA)$ in aqueous media. The first stable reduction product of perchlorate is chlorate. To convert perchlorate to chlorate, two electrons must be supplied, and one oxide ion removed. The highly symmetrical perchlorate ion is resistant either to removal of oxide ion, or to acceptance of electrons, even by solvated electrons in water or in liquid ammonia. This indicates

that suitable electron-acceptor orbitals are high in energy. Perchlorate is readily complexed by α -cyclodextrine but is a poor ligand for cations. Cramer et al, J. Am. Chem. Soc., 89:14, 1967. There are some solids known in which perchlorate is complexed to two metal ions at once (Figure 3. DMAEP is 2-(N-dimethyl)-aminoethyl-pyridine). Lewis et al, Inorg. Chem., 13:147, 1974. In such complexes, the coordinated perchlorate ion has a highly distorted geometry.

A rationalization of these observations is that, in ethanolic solutions, a polymeric form of Ti^{III} binds perchlorate ion in such a way as to distort the perchlorate ion away from tetrahedral symmetry. Electronic rearrangement within that species then results in transfer of two electrons from two Ti^{III} ions to the chlorine center, and concomitant transfer of an oxide ion to titanium. These data are consistent with a gated electron transfer mechanism (Dunn et al, Inorg. Chem., 36:3252-3257, 1997) in which there is distortion of a perchlorate ion by coordination, which has the result of lowering the energy of a chlorine-centered orbital of appropriate symmetry to accept an electron from Ti^{III} .

While the invention has been described in connection with the above examples and illustrations, including those provided in the appended drawings, the scope of the subject invention is only limited by the claims which follow.

What is Claimed is:

1. A catalytic system for enhancing perchlorate ion reduction; wherein the system comprises one or more titanium assemblies, each titanium assembly
5 comprising two or more titanium cations, wherein the cations in the assembly are capable of transferring electrical charge to the perchlorate ion, thereby reducing the oxidation state of the chlorine center of the perchlorate ion, and wherein said titanium cations are in a moderately polar environment.
- 10 2. The catalytic system of Claim 1, wherein the titanium assembly is a dimer of titanium cations.
3. The catalytic system of Claim 1, wherein the moderately polar environment comprises ethyl alcohol.
- 15 4. The catalytic system of Claim 1, wherein the moderately polar environment comprises a non liquid phase comprising a core and a surface, wherein the surface comprises a functional group having an effect on the interaction between the titanium cations and the perchlorate ion approximately the same as the effect of ethyl alcohol.
- 20 5. The catalytic system of Claim 4, wherein the core is hydrophobic.
6. The catalytic system of Claim 4, wherein the core comprises polyvinyl.
- 25 7. The catalytic system of Claim 4, wherein the core comprises silica gel.
8. The catalytic system of Claim 4, wherein the functional group is a hydroxyl group.
- 30 9. The catalytic system of Claim 1, further comprising a ligand in interaction with the titanium assembly.

10. The catalytic system of Claim 9, wherein the ligand comprises a molecule selected from the group consisting of TADP3(COOH)₂; TADP3; 6-amino-6-(4-aminobenzyl)-1,4,8,11 tetraazacyclotetradecane; 1,4,7-triazacyclononane-N,N',N''-triacetic acid; N,N',N'-tris(2-pyridylmethyl)-cic,cis-1,3,5-triaminocyclohexane; α-cyclodextrin; saphyrins and porpherin analogues thereof; HEDTA; DADP3; CYCAPAB.
11. The catalytic system of Claim 4, further comprising a ligand in interaction with the titanium assembly.
12. The catalytic system of Claim 11, wherein the ligand comprises a molecule selected from the group consisting of TADP3(COOH)₂; TADP3; 6-amino-6-(4-aminobenzyl)-1,4,8,11 tetraazacyclotetradecane; 1,4,7-triazacyclononane-N,N',N''-triacetic acid; N,N',N'-tris(2-pyridylmethyl)-cic,cis-1,3,5-triaminocyclohexane; α-cyclodextrin; saphyrins and porpherin analogues thereof; HEDTA; DADP3; and CYCAPAB.
13. The catalytic system of Claim 11, wherein the ligand is immobilized on the surface of the non-liquid phase.
14. A method of reducing perchlorate ions, wherein the method comprises contacting the perchlorate ions with a catalytic system comprising one or more titanium assemblies, each titanium assembly comprising two or more titanium cations, wherein the cations in the assembly are capable of transferring electrical charge to the perchlorate ion, thereby reducing the oxidation state of the chlorine center of the perchlorate ion, and wherein the titanium cations are in a moderately polar environment.
15. The method of Claim 14, wherein the titanium assembly is a dimer of titanium cations.

16. The method of Claim 14, wherein the moderately polar environment comprises ethyl alcohol.
17. The method of Claim 14, wherein the moderately polar environment
5 comprises a non liquid phase comprising a core and a surface, wherein the surface comprises a functional group having an effect on the interaction between the titanium cations and the perchlorate ion approximately the same as the effect of ethyl alcohol.
18. The method of Claim 17, wherein the core is hydrophobic.
- 10 19. The method of Claim 17, wherein the core comprises polyvinyl.
20. The method of Claim 17, wherein the core comprises silica gel.
- 15 21. The method of Claim 17, wherein the functional group is a hydroxyl group.
22. The method of Claim 14, further comprising a ligand in interaction with the titanium assembly.
- 20 23. The method of Claim 22, wherein the ligand comprises a molecule selected from the group consisting of TADP3(COOH)₂; TADP3; 6-amino-6-(4-aminobenzyl)-1,4,8,11 tetraazacyclotetradecane; 1,4,7-triazacyclononane-N,N',N''-triacetic acid; N,N',N''-tris(2-pyridylmethyl)-cis,cis-1,3,5-triaminocyclohexane; α-cyclodextrin; saphyrins and porpherin analogues thereof; HEDTA; DADP3; and
25 CYCAPAB.
24. The method of Claim 17, further comprising a ligand in interaction with the titanium assembly.

25. The method of Claim 24, wherein the ligand comprises a molecule selected from the group consisting of TADP3(COOH)₂; TADP3; 6-amino-6-(4-aminobenzyl)-1,4,8,11 tetraazacyclotetradecane; 1,4,7-triazacyclononane-N,N',N''-triacetic acid; N,N',N'-tris(2-pyridylmethyl)-cis,cis-1,3,5-triaminocyclohexane; α-cyclodextrin; saphyrins and porpherin analogues thereof; HEDTA; DADP3; and CYCAPAB.
26. The method of Claim 14, wherein the ligand is immobilized on the surface of the non-liquid phase.
27. A process of removing perchlorate ions from water, wherein the process comprises reducing perchlorate ions by contacting the perchlorate ions with a catalytic system comprising one or more titanium assemblies, each titanium assembly comprising two or more titanium cations, wherein the cations in the assembly are capable of transferring electrical charge to the perchlorate ion, thereby reducing the oxidation state of the chlorine center of the perchlorate ion, and wherein said titanium cations and perchlorate ion are in a moderately polar environment.
28. A process of removing perchlorate ions from rocket fuel waste, wherein the process comprises reducing perchlorate ions by contacting the perchlorate ions with a catalytic system comprising one or more titanium assemblies, each titanium assembly comprising two or more titanium cations, wherein the cations in the assembly are capable of transferring electrical charge to the perchlorate ion, thereby reducing the oxidation state of the chlorine center of the perchlorate ion, and wherein said titanium cations and perchlorate ions are in a moderately polar environment.
29. The compound 11, 23-dihydroxycarbonyl-25, 26-dihydroxy-3, 7, 15, 19-tetraazatricyclo [19. 3. 1. 19. 13]hexacosa-1(25), 9(26), 10, 12, 21, 23-hexaene or a derivative thereof capable of chelating a titanium assembly having two or more titanium cations.

30. A method of reducing perchlorate ions, wherein the method comprises contacting the perchlorate ions with a catalytic system comprising one or more titanium assemblies, each titanium assembly comprising two or more titanium cations
- 5 in an oxidation state lower than the oxidation state of Ti^{IV} .

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(57) Abstract: The present invention provides a catalytic system for enhancing perchlorate ion reduction. The system includes one or more titanium assemblies, each titanium assembly is formed by two or more titanium cations. The cations in the assembly are capable of transferring electrical charge to the perchlorate ion, thereby reducing the oxidation state of the chlorine center of the perchlorate ion. The electrical charge transfer between the titanium cations and the perchlorate ion is enhanced disposing the titanium cations and the perchlorate ion are in a moderately polar environment.

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**Figure 1. Structure of
Ti(HEDTA)(H₂O)**

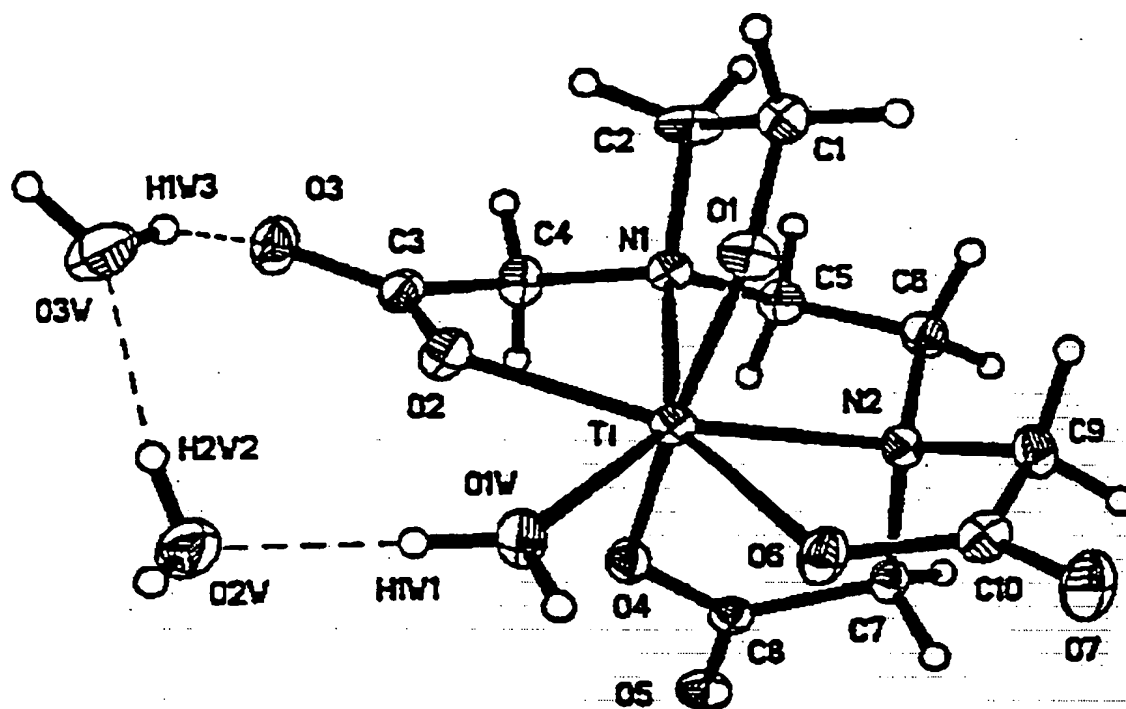


Figure 2 Structure of $\text{Ti}(\text{HEDTA})(\text{H}_2\text{O})^+$

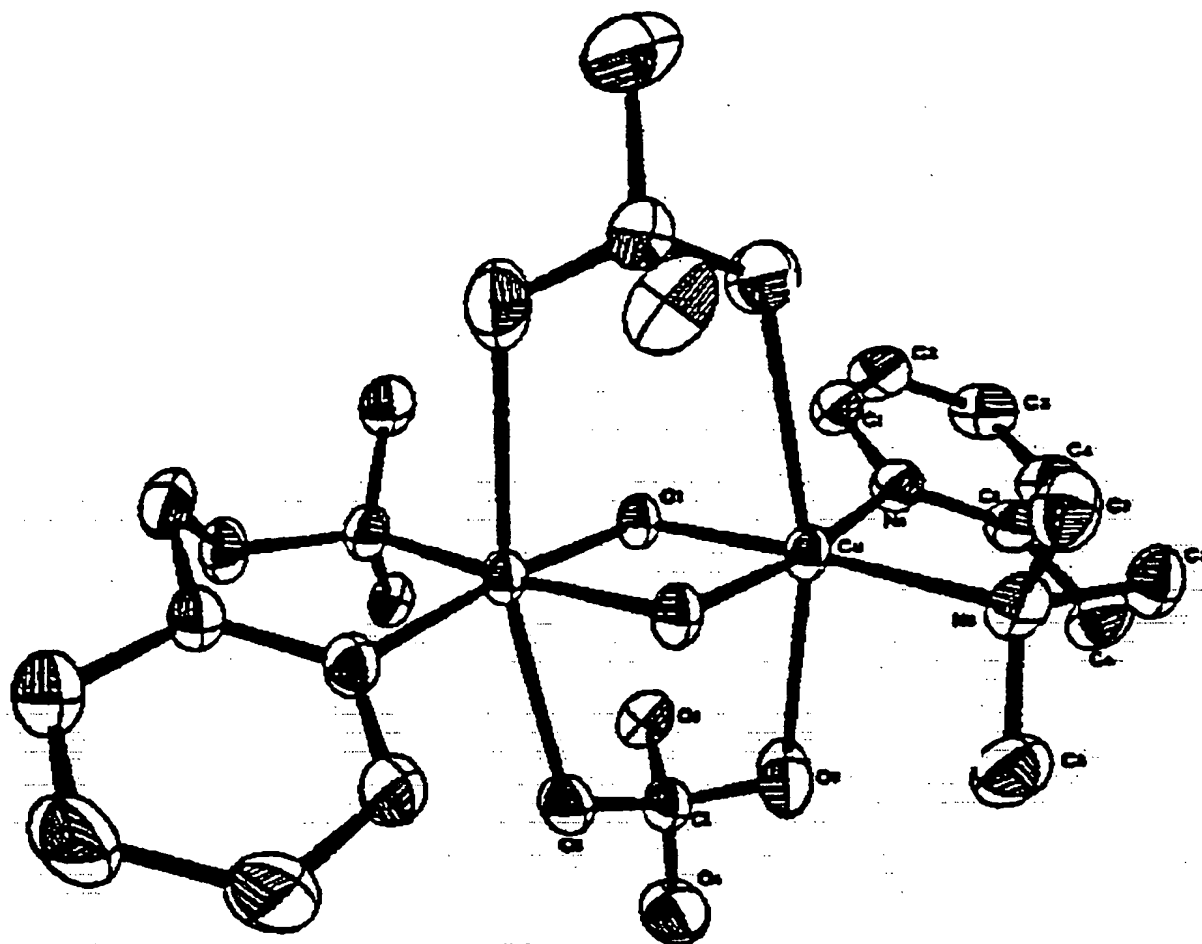


Figure 3. Structure of the complex
 $[\text{Cu}(\text{DMAEP})\text{OH}]_2(\text{ClO}_4)_2$

Lewis, D.L., Hatfield, W.E., Hodgson, D.J.,
Inorg. Chem., 1974, 13, 147

Pecsok, R.L.; Fletcher, A. N *Inorg. Chem.* 1962, 1, 155.

Figure 4

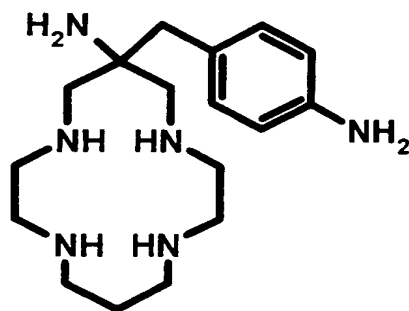
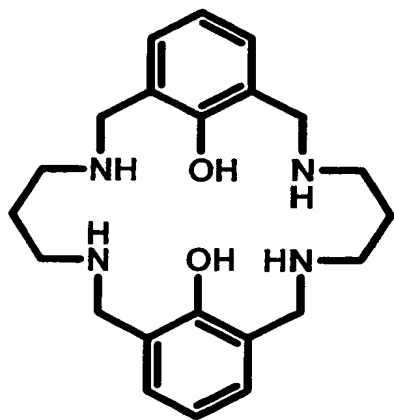
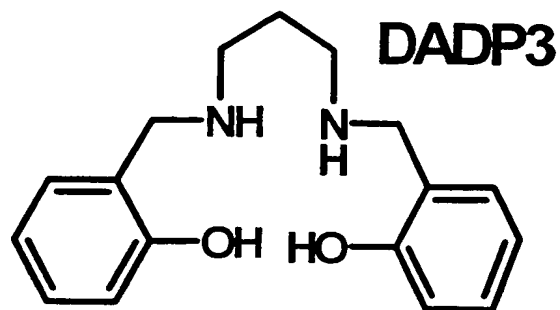
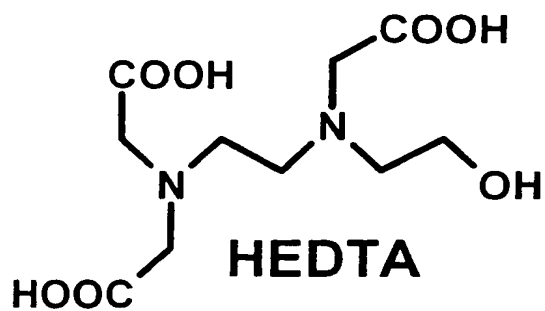


Figure 5

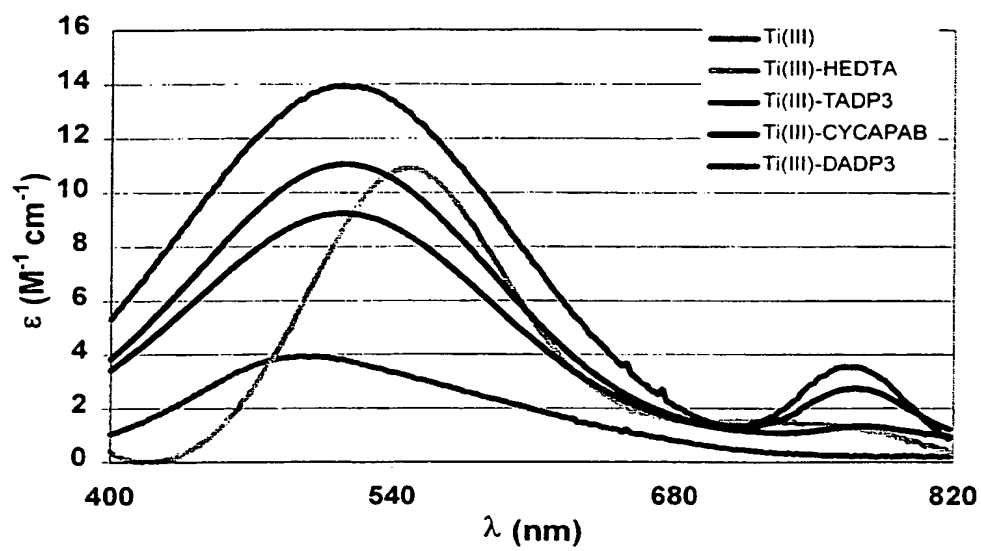
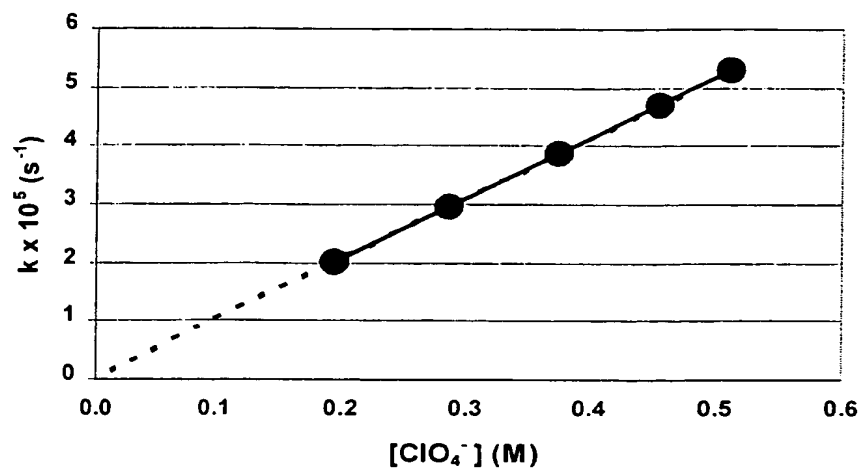
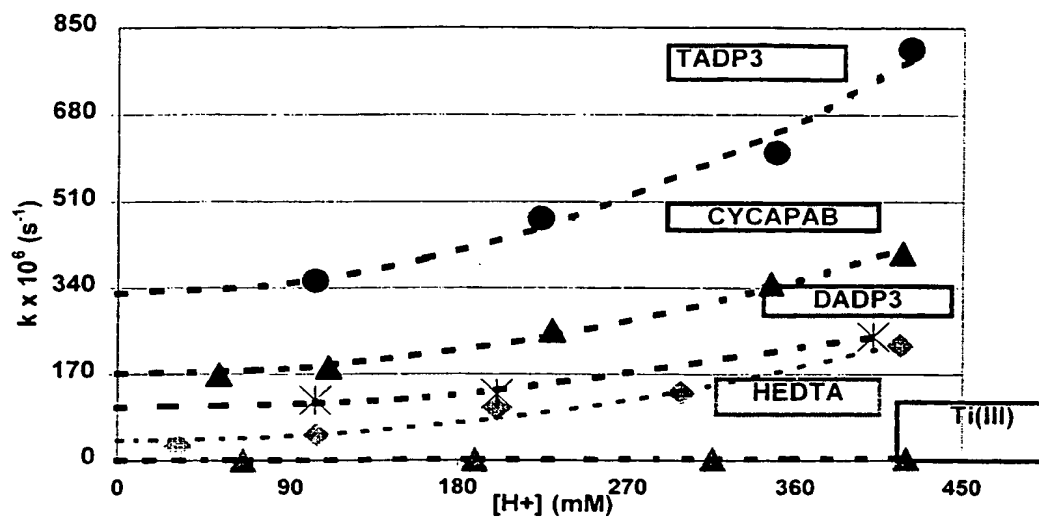


Figure 6



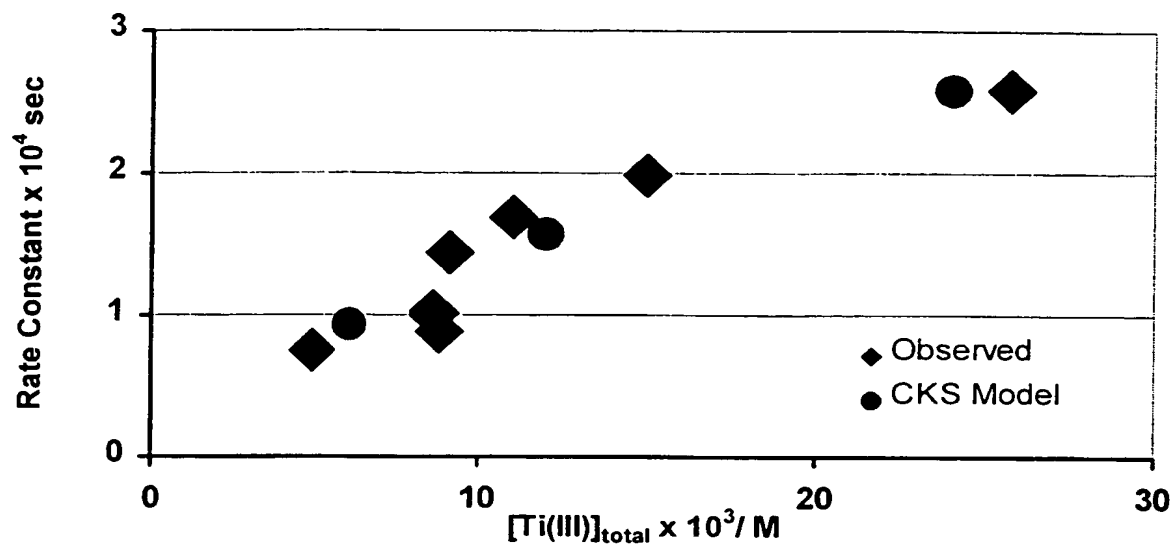
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Figure 7



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Figure 8



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Figure 9

